Kinetics and thermodynamics of thermally reversible polymers

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DOI:
10.33612/diss.136495889

Publication date:
2020

Chapter 5

Implementation of the UNIQUAC model in the OpenCalphad software

In real open source, you have the
right to control your own destiny.

Linus Torvalds

Abstract

The UNIversal QUAsiChemical (UNIQUAC) model is often used, for example in engineering, to obtain activity coefficients in multicomponent systems, while the CALculation of PHAse Diagrams (CALPHAD) method is known for its capability in phase stability assessment and equilibrium calculations. In this work, we combine them by representing the UNIQUAC model according to the CALPHAD method and implementing it in the OpenCalphad software. We explain the harmonization of nomenclature, the handling of the model parameters and the equations and partial derivatives needed for the implementation. The successful implementation is demonstrated with binary and multicomponent phase equilibrium calculations and comparisons with literature data. Additionally we show that the implementation of the UNIQUAC model in the OpenCalphad software allows for the calculation of various thermodynamic properties of the systems considered. The combination provides a convenient way to assess interaction parameters and calculate thermodynamic properties of phase equilibria.

1. This chapter contributes to the paper: **Jing Li**, Bo Sundman, Jozef GM Winkelman*, Antonis I Vakis, Francesco Picchioni, Implementation of the UNIQUAC model in the OpenCalphad software, Fluid Phase Equilibria (2020), 507, 112398.

5.1 Introduction

Generally, in chemical engineering two kinds of thermodynamic models are used: equations of state and models for the excess Gibbs free energy of mixing (Sandler 1986). The models have in common that they contain parameters that have to be adjusted to represent experimental data. The models should be consistent with statistical mechanics (Guggenheim 1952) and thermodynamic constraints (Hillert 2007). Typical earlier models are Margules (Margules 1895), Van Laar (van Laar 1910, van Laar 1913), Redlich-Kister (Redlich and Kister 1948), Scatchard-Hildebrand (Scatchard 1931, Hildebrand and Wood 1933) and Flory-Huggins (Flory 1942, Huggins 1942) equations. In 1964, G.M. Wilson introduced the local composition concept into the excess Gibbs energy model (Wilson 1964). Some well-known models based on this concept are Wilson (Wilson 1964), Non-Random Two-Liquid (NRTL) (Renon and Prausnitz 1968), UNIversal QUAsiChemical (UNIQUAC) (Abrams and Prausnitz 1975), and UNIQUAC Functional-group Activity Coefficients (UNIFAC) (Fredenslund et al. 1975). These are typically used for modeling Vapor-Liquid Equilibrium (VLE), Liquid-Liquid-Equilibria (LLE) and Solid-Liquid-Equilibria (SLE) at relatively low pressures.

Although the mathematical expression of the UNIQUAC model is more complex than that of the NRTL model, UNIQUAC is used more than NRTL in the area of chemical engineering. The reason is that UNIQUAC has fewer adjustable parameters, two instead of three, which are less dependent on temperature, and can be applied to systems with larger size differences. A more detailed overview can be found, for example, in Polling et.al (Polling et al. 2001).

The UNIFAC model (Fredenslund et al. 1975) was published simultaneously with UNIQUAC and is a group-contribution based equivalent of UNIQUAC model. Importantly, UNIFAC is completely predictive, which makes it of great practical value in, for example, the chemical engineering community. The UNIFAC model is based on a growing databank of parameters that are obtained from experimental data. The development of UNIFAC over time is shown in Table 1.4 in chapter 1, which shows that more and more phase equilibrium information and excess thermal properties are included, allowing the number of available functional groups to increase steadily.

In the 1970s, simultaneously with the development of the UNIQUAC and UNIFAC models, CALculation of PHAse Diagrams (CALPHAD)-type models (Kaufman and Bernstein 1970, Hillert and Staffanson 1970) were also developed. Originally, they were mainly used in the fields of inorganic chemistry and metallurgy. Both of these model developments benefited from the availability of computers and have had a strong development during the past 50 years.

The CALPHAD technique is applied to alloys, ceramics and high-temperature processes involving binary, ternary and higher-order systems. Such a system typically includes 10-100 different crystalline phases in addition to gas and liquid phases. Each phase is described with a different Gibbs energy model. CALPHAD includes Long Range Ordering (LRO) for the crystalline phases and Short Range Ordering (SRO) in both solids and liquids. In addition, different kinds of excess model parameters are used to describe the binary, ternary and higher order interaction between the components of a phase. Dealing with so many different phases, a central part of the CALPHAD modeling is an unary database (Dinsdale 1991) where the Gibbs energy for each pure element in each phase is described as a function of temperature, T, relative to reference conditions, up to high temperatures of several thousand kelvin. These Gibbs energy functions are known as lattice stabilities and may include parameters for magnetic ordering. They are needed because an element may dissolve in many different crystalline phases for which the element itself is not stable. Extensive descriptions of CALPHAD models can be found, for example, in Lukas et al. (Lukas et al. 2007), Hillert (Hillert 2007) and Saunders and Miodowski (Saunders and Miodownik 1998). CALPHAD software is able to calculate multicomponent equilibria with hundreds of possible phases and multicomponent phase diagrams. The database contains, in addition to the unary data, model-dependent parameters that depend on the amounts of two, three or more components.

There are several commercial companies marketing software and databases for UNIQUAC/UNIFAC and CALPHAD. OpenCalphad is an open source software (Sundman, Kattner, Palumbo and Fries 2015). CALPHAD applications typically concern the temperatures up to 2000 K whereas UNIQUAC is normally applied at temperatures up to around 400 K. This is one of the main reasons for the different approaches used in the thermodynamic models. However, it is well possible to handle both UNIQUAC and CALPHAD-type models within the same software.

In this work, UNIQUAC is successfully incorporated into OpenCalphad. We show that the combination allows for an easy and accurate calculation of thermodynamic properties and phase diagrams, and the determination of UNIQUAC interaction parameters.

5.2 Exploring the differences between UNIQUAC model and CALPHAD method

There are several significant differences in the use of thermodynamics between UNIQUAC and CALPHAD: the main difference is that the UNIQUAC model has a combinatorial entropy based on the theory of Guggeneim (Guggenheim 1952), taking into account that the components can have very different sizes. In CALPHAD models, on the other hand, the components, normally atoms, have similar sizes and thus an ideal configurational entropy is used. Moreover, CALPHAD can model many crystalline phases simultaneously and takes long-range ordering into account. The use of ideal mixing on each sublattice describes the configurational entropy of complex solid phases with reasonable accuracy. For liquids, there are several models used in CALPHAD to describe short range ordering (Hillert et al. 1985, Pelton et al. 2000), but they do not account for polymerization or polarization.

Another difference is that UNIQUAC models are based on excess Gibbs energy or activity coefficients, whereas the CALPHAD models are always based on a molar Gibbs energy expression; however, as the activity coefficients are calculated from the molar Gibbs energy, this difference is not very important. For applications, a major difference is that CALPHAD software and databases usually consider more than 100 different solid crystalline phases with different molar Gibbs energy models, whereas applications of the UNIQUAC model usually involve few solid phases.

In the CALPHAD method, all models are described using a molar Gibbs energy for each phase and the models can be quite different for different phases. One reason to avoid activity coefficients is that their modeling may cause inconsistencies between the molar Gibbs energy and the chemical potentials.

The integration of both types of models in a single software allows the calculation of equilibria between complex solids described with CALPHAD models and liquids and polymers described with the UNIQUAC model. The free OpenCalphad software (Sundman, Kattner, Palumbo and Fries 2015) was selected because it is publicly available, the source code is open for developing new models and it is written in the new Fortran standard. The OpenCalphad software can perform multicomponent equilibrium calculations and provide all thermodynamic properties of interest, such as enthalpies, entropies, chemical potentials and heat capacities as well as phase diagrams.

5.2.1 The molar Gibbs energy and the molar excess Gibbs energy

In CALPHAD, the molar Gibbs energy for a phase α is expressed as eq. 5.1:

$$G_m^\alpha = \sum_i x_i^\alpha \, {}^\circ G_i^\alpha + RT \sum_i x_i^\alpha \ln(x_i^\alpha) + {}^E G_m^\alpha \tag{5.1}$$

$$x_i^\alpha = \frac{N_i^\alpha}{N^\alpha} \tag{5.2}$$

$${}^E G_m^\alpha = \sum_i \sum_{j>i} x_i^\alpha x_j^\alpha (L_{ij}^\alpha + \sum_{k>j} x_k^\alpha (L_{ijk}^\alpha + \cdots)) \tag{5.3}$$

where the summation over ${}^\circ G_i^\alpha$ represents the contribution from the lattice stabilities explained in section 5.1. The term multiplied with RT is the ideal configurational entropy and ${}^E G_m$ is the excess Gibbs energy. In CALPHAD, it is preferred to use the E as a pre-superscript because the normal superscript position is reserved for the phase label as CALPHAD normally deals with many different phases. The excess Gibbs energy is described by regular solution parameters, L, for binary and higher order interactions which are constants or linearly dependent on the temperature.

The chemical potential of a component i is calculated from the total Gibbs energy for a system:

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}} \tag{5.4}$$

where G is the total Gibbs energy and N_i the number of moles of component i. The chemical potentials are calculated from a molar Gibbs energy by combining the first derivatives of the molar Gibbs energy:

$$\mu_i = G_m + \left(\frac{\partial G_m}{\partial x_i}\right)_{T,P,x_{j\neq i}} - \sum_j x_j \left(\frac{\partial G_m}{\partial x_j}\right)_{T,P,x_{k\neq j}} \tag{5.5}$$

where $G_m = G/N$ is the molar Gibbs energy using mole fractions x_i as composition variables. Temperature, pressure and the other mole fractions are constant when calculating the partial derivatives. This equation is one of the basics in CALPHAD method and derived, for example, in (Lukas et al. 2007, Sundman, Lu and Ohtani 2015). For phases with sublattices, a slightly more complicated equation is needed, as derived in (Sundman and Ågren 1981).

The chemical potential μ_i is expressed using activity coefficients as in all thermodynamics books:

$$\mu_i = {}^{\circ}\mu_i + RT\ln(a_i) \tag{5.6}$$

$$a_i = \gamma_i x_i \tag{5.7}$$

where ${}^{\circ}\mu_i$ is the reference chemical potential, a_i is the activity and γ_i is the activity coefficient describing the deviation from ideality. For an ideal solution, $\gamma_i = 1$.

When the chemical potentials, μ_i, are known, the molar Gibbs energy for a phase α is obtained by a simple summation:

$$G_m^{\alpha} = \sum_i x_i^{\alpha}\mu_i \tag{5.8}$$

The CALPHAD models are typically used for high-temperature systems compared with UNIQUAC model as introduced before and can describe many different types of crystalline phases in addition to liquid and gas phases. In CALPHAD the ideal configurational entropy is normally used but it includes long range ordering in the crystalline phases, separate modeling of the ferromagnetic transition and complex excess models. There is interest to combine calculations using CALPHAD data for calculations at ambient temperatures to study, for example, corrosion with water and other fluids. Most CALPHAD calculations involve systems with *8-10* components and there is a particular unary database that provides data for the pure elements in different crystalline states as well as in liquid and gas species. This makes it possible to combine and extend descriptions of binary and ternary assessments to multicomponent alloys.

In detail CALPHAD always models the integral Gibbs energy, as in eq. 5.1, expressed as a function of temperature and composition using model parameters. The chemical potentials and activity coefficients are derived from this numerically.

Unlike CALPHAD, the UNIQUAC model, developed by Abrams and Prausnitz (Abrams and Prausnitz 1975), is an expression of the molar excess Gibbs energy, g^E. In addition, the activity coefficient of a component i in the liquid, γ_i, is derived from the partial derivative of $n_T \cdot g^E$ with respect to n_i and expressed as (all the symbols are the same as those in the original paper):

$$n_T \cdot g^E = RT\sum_i n_i \ln(\gamma_i) \tag{5.9}$$

$$n_T = \sum_i n_i \tag{5.10}$$

$$RT\ln(\gamma_i) = \left(\frac{\partial n_T \cdot g^E}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{5.11}$$

The derivation of expressions for the activity coefficients starting from eq. 11 is usually tedious and prone to errors. An alternative is to derive the activity coefficients from eqs 5-7. An important difference is that excess Gibbs energy in the UNIQUAC model includes a combinatorial entropy whereas CALPHAD, for substitutional solutions, uses an ideal configurational entropy. This difference will be discussed in detail in section 5.3.

In CALPHAD models, the ideal configurational entropy is modified using sublattices for LRO in crystalline phases. For liquids with strong SRO, such as molten salts or ionic components, there are special models like the 2-sublattice ionic liquid model (Hillert et al. 1985) or the quasichemical model (Pelton et al. 2000). In addition, several excess parameters depending on binary and ternary interactions are used in the excess Gibbs energy in eq. 5.3. Chemical potentials and activity coefficients are calculated by the software using eq. 5.5.

Based on the reasoning so far, it is useful to represent the UNIQUAC model in CALPHAD method and implement it in softwares based on the CALPHAD method, such as, OpenCalphad. Analytical expression of the first partial derivatives of molar Gibbs energy with respect to the components have been implemented in the software. Analytical expressions for the second derivatives are used to speed up convergence (Sundman, Lu and Ohtani 2015), but have no effect on the final calculated results. In this work, we did not implement the analytical expressions for the second derivatives.

5.3 The UNIQUAC model using CALPHAD nomenclature

The UNIQUAC model, derived by Adams and Prausnitz (Abrams and Prausnitz 1975), presents the expression for the excess Gibbs energy as the sum of combinatorial, ${}^{\text{cmb}}G_m$, and residual, ${}^{\text{res}}G_m$, contributions. They are combined into an expression for the molar Gibbs energy, see eqs from 5.12 to 5.18:

$$
\begin{aligned}
G_m &= \sum_i x_i({}^{\circ}G_i + RT\ln(x_i)) + {}^{\text{cmb}}G_m + {}^{\text{res}}G_m && (5.12)\\
{}^{\text{cmb}}G_m &= RT\sum_i x_i \ln(\frac{\Phi_i}{x_i}) + \frac{z}{2}\sum_i x_i q_i \ln(\frac{\theta_i}{\Phi_i}) && (5.13)\\
\Phi_i &= \frac{r_i x_i}{\sum_j r_j x_j} && (5.14)\\
\theta_i &= \frac{q_i x_i}{\sum_j q_j x_j} && (5.15)\\
{}^{\text{res}}G_m &= -RT\sum_i q_i x_i \ln(\rho_i) && (5.16)\\
\rho_i &= \sum_j \theta_j \tau_{ji} && (5.17)\\
{}^{\text{cfg}}G_m &= RT\sum_i x_i \ln(x_i) + {}^{\text{cmb}}G_m && \\
&= RT\sum_i x_i \ln(\Phi_i) + \frac{z}{2}\sum_i x_i q_i \ln(\frac{\theta_i}{\Phi_i}) && (5.18)
\end{aligned}
$$

where q_i is a surface-area parameter and r_i a volume parameter, which are both component structural parameters for constituent i. z is the average number of nearest neighbors of a constituent, always assumed to be 10.

In accordance with the separate excess Gibbs energy terms for the configurational and residual contributions, we calculate the chemical potentials and activity coefficients using eq. 5.5 for each term separately.

$$\gamma_i = \gamma_i^c \gamma_i^r \tag{5.19}$$

$$\ln(\gamma_i) = \ln(\gamma_i^c) + \ln(\gamma_i^r) \tag{5.20}$$

where γ_i^c and γ_i^r represent the combinatorial and the residual contributions to the activity coefficients, respectively.

5.3.1 The configurational Gibbs energy in the UNIQUAC model

Abrams and Prausnitz (Abrams and Prausnitz 1975) derived the configurational activity coefficient from Guggenheim (Guggenheim 1952) taking into account that the components usually have different interaction surfaces, q_i, and volumes, r_i. We start from the configurational molar Gibbs energy, ${}^{\text{cfg}}G_m$, eq. 5.18, based on the UNIQUAC model including the ideal term:

$$\begin{aligned} {}^{\text{cfg}}G_m &= RT\sum_i x_i \ln(x_i) + {}^{\text{cmb}}G_m \\ &= RT\sum_i x_i \left[\ln(\Phi_i) + \frac{z}{2} q_i \ln(\frac{\theta_i}{\Phi_i})\right] \end{aligned} \tag{5.21}$$

The auxiliary function f is defined to simplify the calculations below:

$$f = \frac{{}^{\text{cfg}}G_m}{RT} = \sum_i x_i \left\{\ln(\Phi_i) + \frac{z}{2} q_i \left[\ln(\theta_i) - \ln(\Phi_i)\right]\right\} \tag{5.22}$$

where, by definition, $\sum_i \Phi_i = \sum_i \theta_i = \sum_i x_i = 1$ and f is independent of temperature.

The first derivative of the configurational Gibbs energy

The derivative of ${}^{\text{cfg}}G_m/RT$ with respect to x_k is:

$$\begin{aligned} \frac{1}{RT}\frac{\partial\, {}^{\text{cfg}}G_m}{\partial x_k} &= \left[\ln(\Phi_k) + \frac{z}{2} q_k \ln(\frac{\theta_k}{\Phi_k})\right] \\ &\quad + \sum_i x_i \left[\frac{1}{\Phi_i}\frac{\partial \Phi_i}{\partial x_k} + \frac{z}{2} q_i (\frac{1}{\theta_i}\frac{\partial \theta_i}{\partial x_k} - \frac{1}{\Phi_i}\frac{\partial \Phi_i}{\partial x_k})\right] \end{aligned} \tag{5.23}$$

From this we obtain (see Appendix 6.15):

$$\begin{aligned} \frac{1}{RT}\frac{\partial\, {}^{\text{cfg}}G_m}{\partial x_k} &= \ln(\Phi_k) + 1 - \frac{r_k}{\sum_j x_j r_j} \\ &\quad + \frac{z}{2}\left[q_k \ln(\frac{\theta_k}{\Phi_k}) + q_k(\frac{\Phi_k}{\theta_k} - 1) - \sum_i x_i q_i (\frac{\Phi_i}{\theta_i} - 1)\right] \end{aligned} \tag{5.24}$$

The section "Derivatives of the configurational part" in the Appendix shows that inserting eqs 5.18 and 5.24 in eq. 5.5 results in a chemical potential which reproduces the configurational activity coefficient from (Abrams and Prausnitz 1975). The chemical potentials can also be used to recover the molar Gibbs energy using eq. 5.8. The derivatives of ${}^{cfg}G_m/RT$ with respect to T and P are zero.

The second derivative of the configurational Gibbs energy

The numerical procedure in OpenCalphad requires also the second derivatives with respect to the mole fractions:

$$\begin{aligned}\frac{1}{RT}\frac{\partial^2({}^{\mathrm{cfg}}G_m)}{\partial x_k \partial x_l} &= -\frac{\Phi_l}{x_l} + \frac{\Phi_k\Phi_l}{x_k x_l} + \frac{z}{2}q_k\frac{\Phi_l}{x_l} - \frac{z}{2}q_l\theta_l\frac{\Phi_k}{x_k} \\ &\quad + \frac{z}{2}q_l\frac{\Phi_k}{x_k} - \frac{z}{2}\frac{\Phi_l}{x_l}\frac{\sum_j x_j q_j}{\sum_j x_j r_j} \qquad (5.25)\end{aligned}$$

as shown in Appendix 6.15.

5.3.2 The residual part of the UNIQUAC model

The residual integral Gibbs energy expression from Abrams and Prausnitz (Abrams and Prausnitz 1975) is denoted ${}^{\mathrm{res}}G_m/RT$ in the CALPHAD method and written as:

$$\frac{{}^{\mathrm{res}}G_m}{RT} = -\sum_i x_i q_i \ln(\rho_i) \qquad (5.26)$$

$$\rho_i = \sum_j \theta_j \tau_{ji} \qquad (5.27)$$

$$\tau_{ji} = \exp(-\frac{u_{ji} - u_{ii}}{RT}) \qquad (5.28)$$

where $\Delta u_{ji} = u_{ji} - u_{ii}$ and u_{ii} is a property of the pure component. This means that, in the general case, $\Delta u_{ij} \neq \Delta u_{ji}$ and also $\tau_{ij} \neq \tau_{ji}$. We introduce a new symbol, w_{ji} with dimension K to describe τ_{ji}:

$$w_{ji} = \frac{u_{ji} - u_{ii}}{R} \qquad (5.29)$$

$$\tau_{ji} = \exp(-\frac{w_{ji}}{T}) \qquad (5.30)$$

The first order partial derivatives of residual Gibbs energy to component concentration and temperature are:

$$\frac{1}{RT}\frac{\partial\, {}^{\mathrm{res}}G_m}{\partial x_k} = q_k\left[1 - \ln(\rho_k) - \sum_i \frac{\theta_i \tau_{ki}}{\rho_i}\right] \qquad (5.31)$$

$$\begin{aligned}\frac{1}{RT}\frac{\partial\, {}^{\mathrm{res}}G_m}{\partial T} &= -\sum_i \frac{x_i q_i}{\rho_i}\sum_j \theta_j \frac{\partial \tau_{ji}}{\partial T} \\ &= -\sum_i \frac{x_i q_i}{\rho_i}\sum_j \theta_j w_{ji} T^{-2}\tau_{ji} \qquad (5.32)\end{aligned}$$

The second order partial derivatives are:

$$\frac{1}{RT}\frac{\partial^2\left({}^{\mathrm{res}}G_m\right)}{\partial x_k \partial x_l} = \frac{q_k q_l}{\sum_j x_j q_j}\left(1-\frac{\tau_{lk}}{\rho_k}-\frac{\tau_{kl}}{\rho_l}+\sum_i \frac{\theta_i \tau_{ki}\tau_{li}}{\rho_i^2}\right) \tag{5.33}$$

$$\begin{aligned}
\frac{1}{RT}\frac{\partial^2\left({}^{\mathrm{res}}G_m\right)}{\partial T^2} &= -\sum_i \frac{x_i q_i}{\rho_i}\sum_j \theta_j \frac{\partial^2 \tau_{ji}}{\partial T^2} + \sum_i \frac{x_i q_i}{\rho_i^2}\left(\sum_j \theta_j \frac{\partial \tau_{ji}}{\partial T}\right)^2 \\
&= -\sum_i \frac{x_i q_i}{\rho_i}\sum_j \theta_j \left[-2\frac{\Delta u_{ji}}{RT^3}+\left(\frac{\Delta u_{ji}}{RT^2}\right)^2\right]\tau_{ji} \\
&\quad +\sum_i \frac{x_i q_i}{\rho_i^2}\left(\sum_j \theta_j \frac{\Delta u_{ji}}{RT^2}\tau_{ji}\right)^2
\end{aligned} \tag{5.34}$$

$$\begin{aligned}
\frac{1}{RT}\frac{\partial^2\left({}^{\mathrm{res}}G_m\right)}{\partial x_k \partial T} &= -\frac{q_k}{\sum_j \theta_j \tau_{jk}}\sum_j \theta_j \frac{\partial \tau_{jk}}{\partial T} - q_k \sum_i \frac{\theta_i}{\sum_j \theta_j \tau_{ji}}\frac{\partial \tau_{ki}}{\partial T} \\
&\quad + q_k \sum_i \frac{\theta_i \tau_{ki}}{\left(\sum_j \theta_j \tau_{ji}\right)^2}\sum_j \theta_j \frac{\partial \tau_{ji}}{\partial T} \\
&= -\frac{q_k}{\sum_j \theta_j \tau_{jk}}\sum_j \theta_j \frac{\Delta u_{jk}}{RT^2}\tau_{jk} - q_k \sum_i \frac{\theta_i}{\sum_j \theta_j \tau_{ji}}\frac{\Delta u_{ki}}{RT^2}\tau_{ki} \\
&\quad + q_k \sum_i \frac{\theta_i \tau_{ki}}{\left(\sum_j \theta_j \tau_{ji}\right)^2}\sum_j \theta_j \frac{\Delta u_{ji}}{RT^2}\tau_{ji}
\end{aligned} \tag{5.35}$$

More detailed mathematical derivations are shown in Appendix 6.16.

In order to confirm the consistency between chemical potential and Gibbs energy in the UNIQUAC model, eq. 5.5 is rearranged as:

$$\begin{aligned}
\mu_i &= G_m + \left(\frac{\partial G_m}{\partial x_i}\right)_{T,P,x_{j\neq i}} - \sum_j x_j \left(\frac{\partial G_m}{\partial x_j}\right)_{T,P,x_{k\neq j}} \\
&= \left(G_m^{ideal} + \frac{\partial G_m^{ideal}}{\partial x_i} - \sum_j x_j \frac{\partial G_m^{ideal}}{\partial x_j}\right) + \left(G_m^{E,c} + \frac{\partial G_m^{E,c}}{\partial x_i} - \sum_j x_j \frac{\partial G_m^{E,c}}{\partial x_j}\right) \\
&\quad + \left(G_m^{E,r} + \frac{\partial G_m^{E,r}}{\partial x_i} - \sum_j x_j \frac{\partial G_m^{E,r}}{\partial x_j}\right) \\
&= \mu_i^{ideal} + \mu_i^{E,c} + \mu_i^{E,r} \\
&= RT\ln x_i + RT\ln \gamma_i^c + RT\ln\gamma_i^r
\end{aligned} \tag{5.36}$$

The residual contribution to the chemical potential or the activity coefficient has been calculated by summing the first derivatives of ${}^{\mathrm{res}}G_m/RT$ according to eq. 5.5 and it is shown to be the same as the equation in Abrams' paper (Abrams and Prausnitz 1975). For more detailed mathematical derivations, see Appendix 6.17.

5.4 Equilibrium calculations

In chemical engineering, especially in the separation of multicomponent mixtures, the objective of phase equilibrium calculations are equilibrium compositions of different phases. The compositions and thermodynamic properties in multicomponent multiphase system can be calculated by various methods. With a model that provides the chemical potentials, or the activity coefficients, of the components, the equilibrium is calculated by finding the composition of the phases that gives the same chemical potentials of each component in all stable phases. This is usually a rapid and stable method if the set of stable phases is known beforehand, and has been used for the UNIQUAC model. In the CALPHAD method, the calculations sometimes involve hundreds of phases, and determining the set of stable phases is a major problem.

CALPHAD uses a Gibbs Energy Minimization (GEM) technique (Eriksson 1971, Hillert 1981, Sundman, Lu and Ohtani 2015), taking into account all possible phases and then determining the set of phases and their compositions that give the lowest Gibbs energy. At this minimum, the components have the same chemical potential in each stable phase.

The OpenCalphad software uses an algorithm described in (Sundman, Lu and Ohtani 2015) and requires a model for the molar Gibbs energy. The algorithm also requires that the first and second derivatives of the Gibbs energy with respect to temperature, pressure and all constituents are implemented in the software in order to find the equilibrium in a fast and efficient way.

However, the situation for the UNIQUAC model is totally different. Previous attempts to use the Gibbs minimization technique to calculate equilibria with the UNIQUAC model (Iglesias-Silva et al. 2003, Rocha and Guirardello 2009, Rossi et al. 2009) have been limited to binary and ternary systems. Some have used linear programming techniques which rely on the possibility to calculate the chemical potentials in each stable phase separately (Rocha and Guirardello 2009, Rossi et al. 2009). This is in fact different from to the idea of a Gibbs energy minimization, in which the set of stable phases is not known a priori because the method is more or less identical to equating the chemical potentials of the components in a preselected set of stable phases. The algebraic method developed by Iglesias-Silva et al. (Iglesias-Silva et al. 2003) can calculate phase equilibrium for any number of components and phases and their eq. 4 is similar to eq. 5.5 in this paper. However, their mathematical method to calculate the equilibrium is not generalized to multiphase systems and they have not introduced the entropy of mixing in their equations.

Talley et al. (Talley et al. 1992) compared UNIQUAC and CALPHAD modeling techniques. They claim significantly better fit to experimental data using CALPHAD excess models, with an ideal mixing of the components with the FactSage (Bale et al. 2009) software.

Therefore, combining the CALPHAD and UNIQUAC methods opens up possibilities for better equilibrium calculations and the exchange of ideas and experiences about models and methods between the CALPHAD and UNIQUAC communities. With the OpenCalphad software, this combination is now possible.

At present, only calculations for LLE are shown in this paper. The reason is that, in OpenCalphad, it is necessary to define a reference state for each element and provide a Gibbs energy function for each element or molecule relative to this reference state in each phase, gas, liquid and solid. It is possible to introduce either fugacities or non-ideal gas models, but, for calculations with several phases, these data must be introduced in a consistent way.

Table 5.1: Structural parameters (q and r) used in the calculations

liquid	q	r
water	1.4	0.92
2,2,4-trimethylpentane	5.008	5.846
acetonitrile	1.72	1.87
aniline	2.83	3.72
benzene	2.40	3.19
methylcyclopentane	3.01	3.97
n-heptane	4.40	5.17
n-hexane	3.86	4.50
n-octane	4.93	5.84

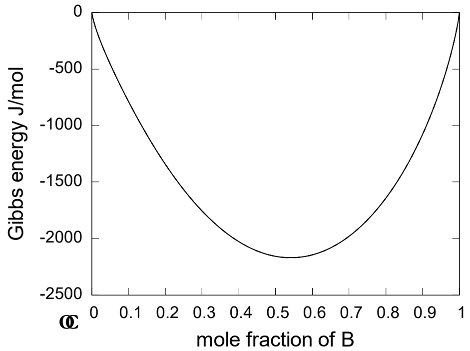
5.5 Results

The equations for the Gibbs energy calculation that include the contributions from UNIQUAC were translated into a Fortran script and added into the OpenCalphad software. This code is publicly accessible (`http://www.opencalphad.com`). This section is used to confirm the successful implementation of the UNIQUAC model in this software. First, the implementation of the UNIQUAC model in the OpenCalphad software is confirmed for artificial systems. Second, it is used to calculate thermodynamic properties and phase diagrams for binary, ternary, and quaternary systems. In the end, its ability to assess interaction parameters of a ternary system is tested. All the systems in this section were chosen from the open literature.

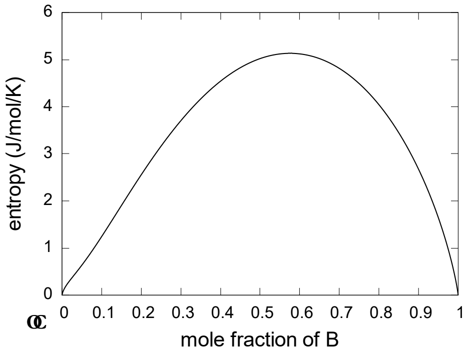
5.5.1 Initial tests of the implementation

In order to verify the implementation of the UNIQUAC model in the OpenCalphad software, two steps are performed in this work. First, the implementation of the combinatorial excess Gibbs energy in the UNIQUAC model is tested by comparison of calculated results of thermodynamic properties obtained by Fortran code implemented in OpenCalphad, and that written independently based on the UNIQUAC model. In these calculations, structure parameters, $q(A) = 1.4$, $r(A) = 0.92$, $q(B) = 4.93$, and $r(B) = 5.84$, are used. The results are shown in Fig. 5.1. From this figure, we conclude that OpenCalphad calculates the combinatorial excess Gibbs energy according to the UNIQUAC model correctly.

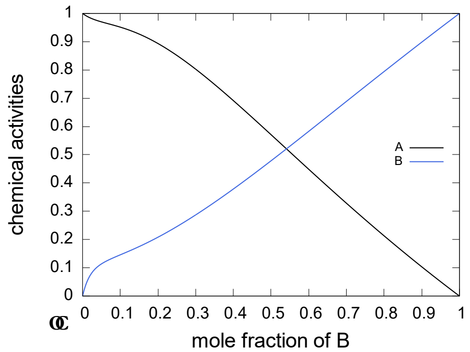
Second, the residual part of the UNIQUAC model was implemented in OpenCalphad along with the combinatorial part. In order to verify the complete implementation of the UNIQUAC model, Fig. 4 of Abrams and Prausnitz (Abrams and Prausnitz 1975) is reproduced here as it presents three typical situations in binary liquid-liquid systems: soluble ($q_1 = q_2 = 2$), critical state between soluble and insoluble ($q_1 = q_2 = 2.5$), and partially soluble with a miscibility gap ($q_1 = q_2 = 3$). The Gibbs energy curves as function of composition were calculated for three different sets of values of q using $r_1 = r_2 = 3.3$ and $\tau_{12} = \tau 21 = exp(-180/T)$ at 400 K. The results are shown in Fig. 5.2(a) and confirm the successful implementation. The miscibility gap for the system with $q_1 = q_2 = 3$ is shown in Fig. 5.2(b).



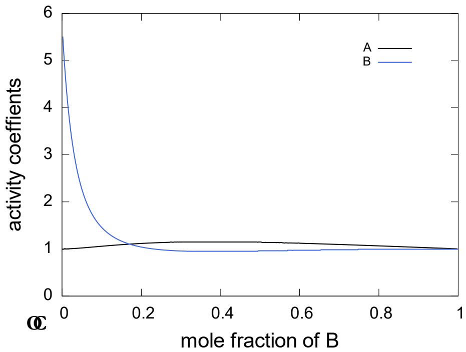
(a) Gibbs energy



(b) entropy

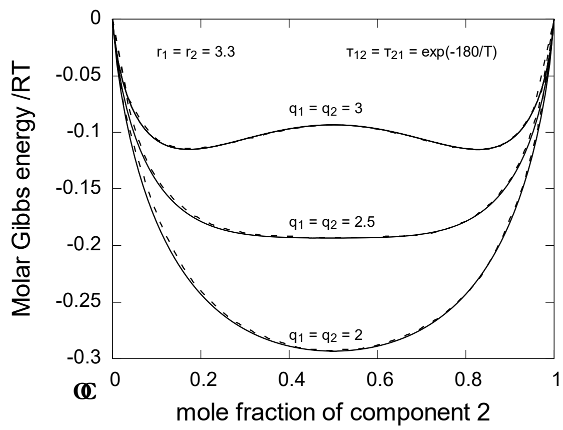


(c) chemical activites

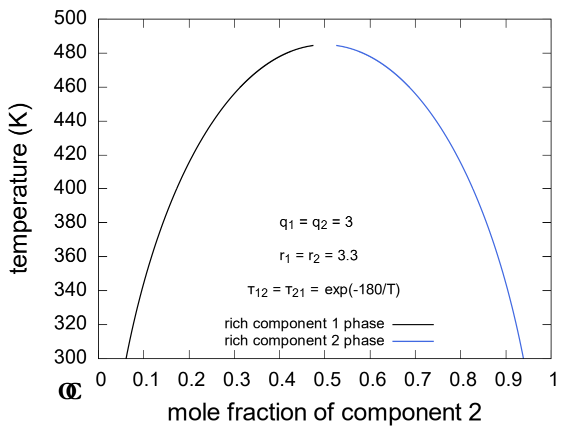


(d) activity coefficients

Figure 5.1: Comparison of thermodynamic properties obtained by implementation of the combinatorial excess Gibbs energy of the UNIQUAC model in OpenCalphad and those obtained directly from UNIQUAC calculations (overlapping). $q(A) = 1.4$, $r(A) = 0.92$, $q(B) = 4.93$, and $r(B) = 5.84$. (a): Gibbs energy; (b): entropy; (c): activities; (d): activity coefficients.

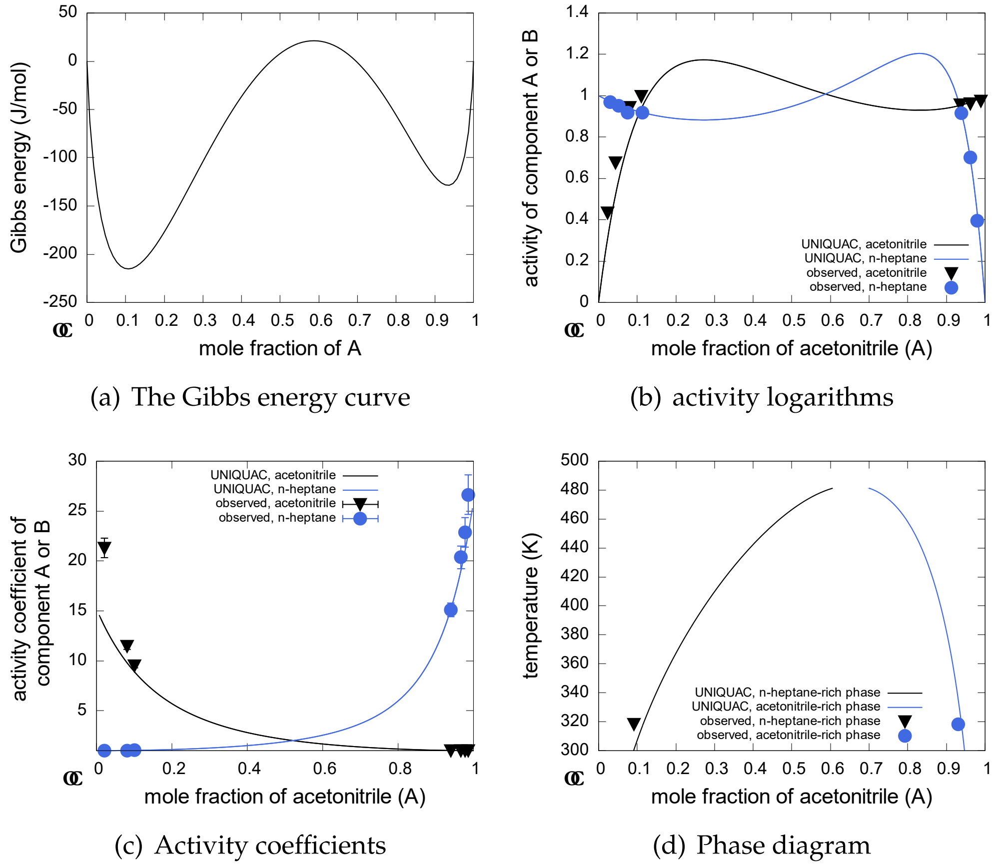


(a) Gibbs energy curves



(b) Phase diagram

Figure 5.2: (a): Gibbs energy curves for various values of q with $r_1 = r_2 = 3.3$ and $\tau_1 = \tau_2 = exp(-180/T)$. Solid lines: calculated by the UNIQUAC model implemented in OpenCalphad software and dash lines are extracted from Fig. 4 in Abrams and Prausnitz (Abrams and Prausnitz 1975). (b): Calculated miscibility gap vs. temperature for the Gibbs energy curve with $q_1 = q_2 = 3$.



(a) The Gibbs energy curve

(b) activity logarithms

(c) Activity coefficients

(d) Phase diagram

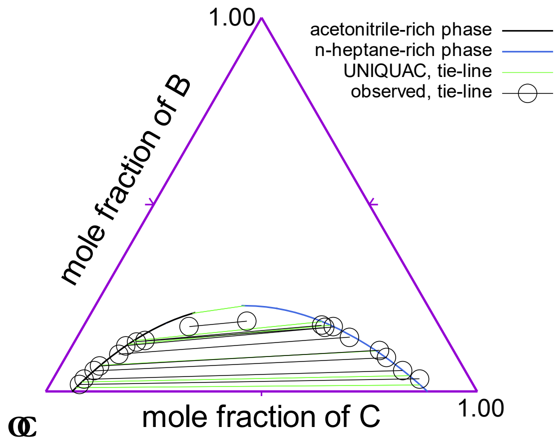
Figure 5.3: Thermodynamic calculations for the binary system acetonitrile(A)-n-heptane(B). Solid lines: calculated by the UNIQUAC model implemented in the OpenCalphad software. Symbols: data of Palmer et.al (Palmer and Smith 1972). (a): the Gibbs energy; (b): activities; (c): activity coefficients; (d): isobar phase diagram. (a)-(c) obtained at 318 K.

5.5.2 Calculation of binary systems

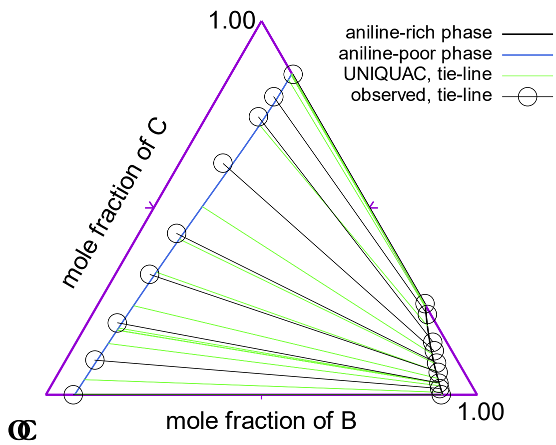
The implementation of the UNIQUAC model in the OpenCalphad software is tested for its capability to calculate the miscibility gap in the liquid phase using the system acetonitrile (A) - n-heptane (B). The calculations are based on the binary interaction parameters in the Table 5.2 and compared to the experimental data of Palmer et.al. (Palmer and Smith 1972). The results are shown in Fig. 5.3. The miscibility gap is evident from the Gibbs energy curve, see Fig. 5.3(a) and the fact that the chemical potentials have a minimum and a maximum, see Fig. 5.3(b). The activity coefficients and the miscibility gap as a function of temperature have also been calculated, see Fig. 5.3(c) and 5.3(d). Again, good agreement is obtained between the experimental and calculated data, illustrating the ability of the implementation of the UNIQUAC model in OpenCalphad to calculate phase equilibria in binary liquid-liquid systems.

5.5.3 Calculation of ternary systems

In industrial processes, two types of ternary systems with partial miscibility are of interest. If there is one partially miscible binary, the ternary system is defined as type I; if there are two partially miscible binaries, the ternary system is defined as type II (Fuchs et al. 1983). To illustrate these types of partial miscibility, we selected two ternary systems: acetonitrile-benzen-n-heptane (type I) and n-hexane-aniline-methylcyclopentane (type II). Their isothermal phase diagrams are calculated by the implemented UNIQUAC model in the OpenCalphad software and compared with experimental data (Palmer and Smith 1972, Darwent and Winkler 1943), see Fig. 5.4. The interaction parameters for the calculations are taken from Tables 5.1 and 5.2.



(a)



(b)

Figure 5.4: Calculated isothermal phase diagram for ternary systems. (a): acetonitrile(A)-n-heptane(B)-benzen(C) at 318.15 K (Palmer and Smith 1972). (b): n-heptane(A)-aniline(B)-methylcyclopentane(C) at 298.15 K (Darwent and Winkler 1943).

Generally, the miscibility gap of a binary or multicomponent liquid system changes with temperature. Based on the parameters in Tables 5.1 and 5.2, phase diagrams for the ternary system acetonitrile(A)-n-heptane(B)-benzen(C) at five different temperatures are calculated with the UNIQUAC model implemented in the OpenCalphad software. Figure 5.5 shows that the miscibility gap closes at higher temperature. These results are in agreement with the reference results obtained by Y.C. Kim et.al. (Kim et al. 1996).

Table 5.2: The residual parameters for the ternary and quaternary systems taken from (Abrams and Prausnitz 1975) and (Anderson and Prausnitz 1978)

System	w_{12}	w_{21}	w_{13}	w_{31}	w_{14}	w_{41}	w_{23}	w_{32}	w_{24}	w_{43}	w_{34}	w_{43}
Acetonitrile(1) N-Heptane(2) Benzene(3)	23.71	545.71	60.28	89.57	-	-	245.42	-135.93				
N-Heptane(1) Aniline(2) Methylcyclopentane(3)	283.76	34.82	-138.84	162.13	-	-	54.36	228.71				
2,2,4-Trimethylpentane(1) Furfural(2) Cyclohexane(3) Benzene(4)	410.08	-4.98	141.01	-112.66	80.91	-27.13	41.17	354.83	71.00	12.00	73.79	82.20

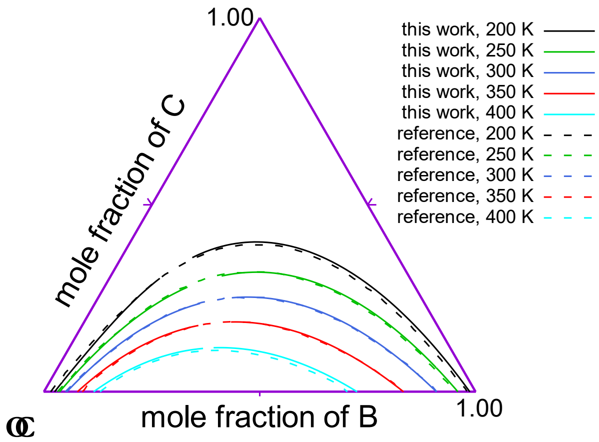


Figure 5.5: Temperature dependency of isothermal sections for the ternary system acetonitrile(A)-n-heptane(B)-benzen(C) calculated at 200 , 250 , 300 , 350 and 400 K using the parameters in Tables 5.1 and 5.2. Solid lines: calculated in this work; dash lines: calculated in literature (Kim et al. 1996).

5.5.4 Calculation of quaternary system

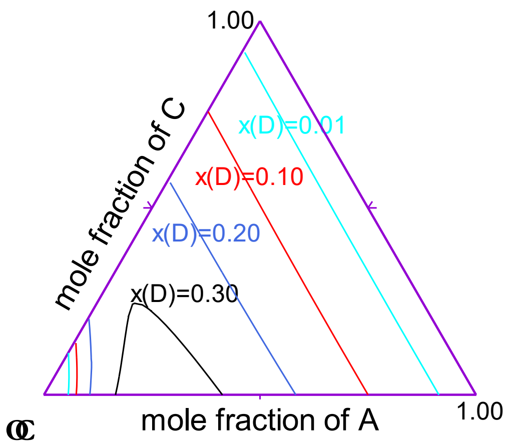


Figure 5.6: Isothermal isopleth for the system 2,2,4-trimethylpentane(A) - furfural(B) - cyclohexane(C) - benzene(D) at several benzene mole fraction.

In order to confirm the possibility to calculate phase equilibria in multicomponent systems, an isothermal isopleth of the quaternary system 2,2,4-trimethylpentane(A) - furfural(B) - cyclohexane(C) - benzene(D) is plotted in Fig. 5.6 at benzene mole fractions of 0.01 , 0.10 , 0.20 and 0.25 . At low benzene mole fractions, there is a miscibility gap across the system from the 2,2,4-trimethylpentane-furfural binary to the furfural - 2,2,4-trimethylpentane binary. At higher benzene contents, the miscibility gap closes from the 2,2,4-trimethylpentane-furfural side. Note that there are no tie-lines in Fig. 5.6 because one end of the tie-line is not in the plane of the diagram.

5.5.5 Assessment of a ternary system

The previous subsections illustrate the successful implementation of the UNIQUAC model in OpenCalphad. The motivation of this work is to assess the interaction parameters and to calculate thermodynamic properties and phase equilibria in chemical engineering applications. In this subsection, we explore the possibility to assess the binary interaction parameters of a ternary system using the UNIQUAC model implemented in OpenCalphad, to predict the isothermal phase equilibria of the system, and then to compare the results with literature data. For this purpose, we use the ternary system acetonitrile (A) - benzene (B) - n-heptane (C).

Table 5.3 compares three sets of parameters. The first set is taken from literature (Anderson and Prausnitz 1978). The other two sets are the parameter estimations of this work. The difference between these two sets of parameters is the different weight assigned to the experimental enthalpy data in the binary system, benzene (B) - n-heptane (C), because of the inconsistency between excess enthalpy and activity coefficient data (vide infra). The Normalized Sum of Squared Errors (NSSE) was used as a measure of the goodness of the assessment for the three sets of parameters. The parameter set obtained with assessment 2 resulted in the lowest NSSE, see Table 5.4. However, it is also important to consider the quality of the prediction of the ternary isothermal section, which will be discussed below.

Table 5.3: Binary interaction parameters for the system acetonitrile (A) - benzene (B) - n-heptane (C), assessed by (Anderson and Prausnitz 1978) and obtained in this work.

parameter type	a_{AB}	a_{BA}	a_{AC}	a_{CA}	a_{BC}	a_{CB}
literature[a]	60.28	89.57	23.71	545.71	-135.93	245.42
assessment 1[b]	102.58	52.55	23.71	545.71	32.70	58.94
assessment 2[c]	102.58	52.55	23.71	545.71	46.66	63.50

a reference: (Anderson and Prausnitz 1978).

b: weight 0 is assigned to enthalpy experimental data in this work.

c: weight 0.5 is assigned to enthalpy experimental data in this work.

Binary systems

The interaction parameters of acetonitrile (A) - benzene (B) are assessed based on experimental data (Srivastava and Smith 1986, Nagata and Gotoh 1996, Nagata and Nakamura 1987, Nagata et al. 1982, Absood et al. 1976, Palmer and Smith 1972, Brown

Table 5.4: Normalized Sum of Squared Errors (NSSE) of three sets of parameters listed in Table 5.3.

system	number of data points	number of parameters	NSSE literature	NSSE assessment 1	NSSE assessment 2
AB[a]	245	2	15.0230	6.0917	6.0917
AC[b]	30	2	2.6842	2.6842	2.6842
BC[c]	59	2	3026.0000	256.2602	175.9777

a: reference: (Palmer and Smith 1972, Srivastava and Smith 1986, Nagata and Gotoh 1996)
(Nagata and Nakamura 1987, Nagata et al. 1982, Absood et al. 1976, Brown and Fock 1956, Di Cave et al. 1980)

b: reference: (Palmer and Smith 1972)

c: reference: (Nagata and Nakamura 1987, Lundberg 1964, Palmer and Smith 1972)

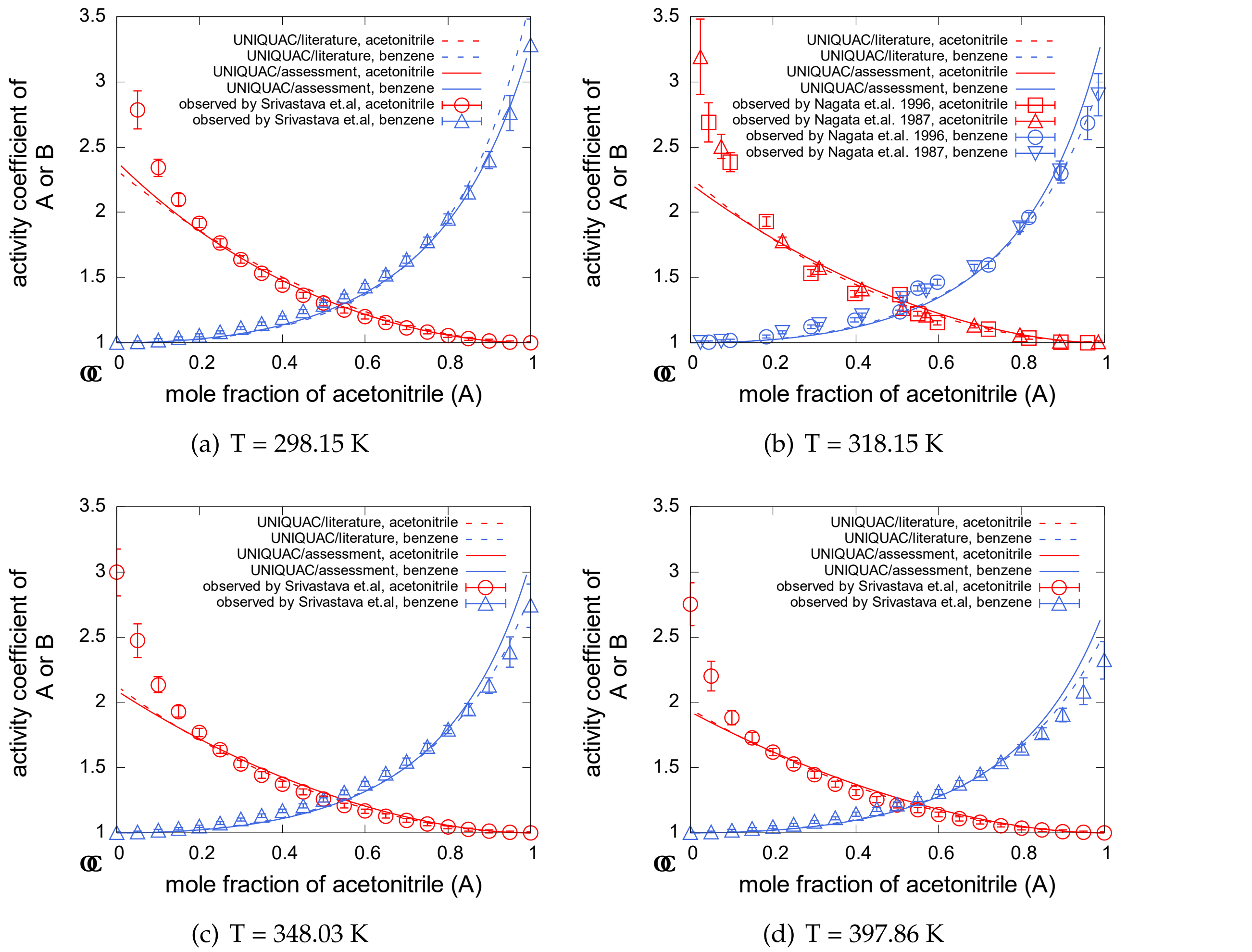
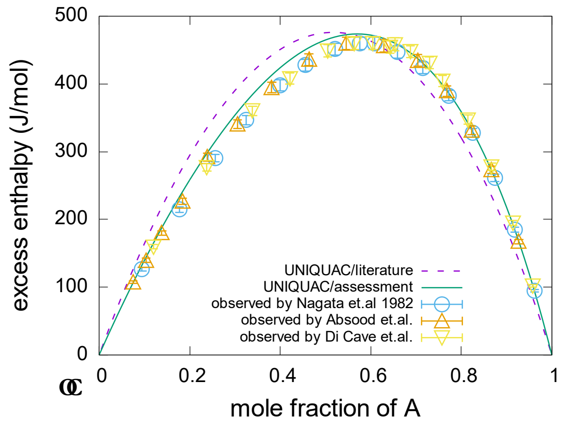
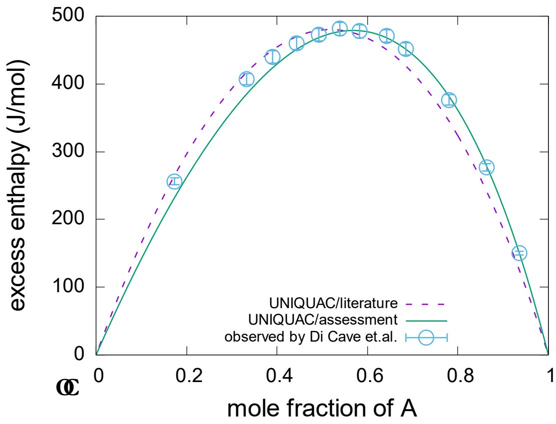


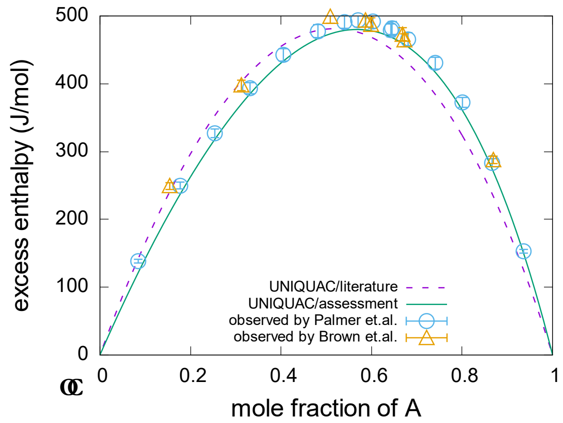
Figure 5.7: Activity coefficients of component acetonitrile or benzene for the binary system acetonitrile (A) - benzene (B) at four different temperatures. Solid lines: calculated by OpenCalphad software with parameters assessed in this work, see Table 5.3; dash lines: calculated with parameters assessed by literature (Anderson and Prausnitz 1978), see Table 5.3; symbols: experimental data observed by Srivastava et.al and Nagata et.al. (Srivastava and Smith 1986, Nagata and Gotoh 1996, Nagata and Nakamura 1987).



(a) T = 298.15 K



(b) T = 314.35 K



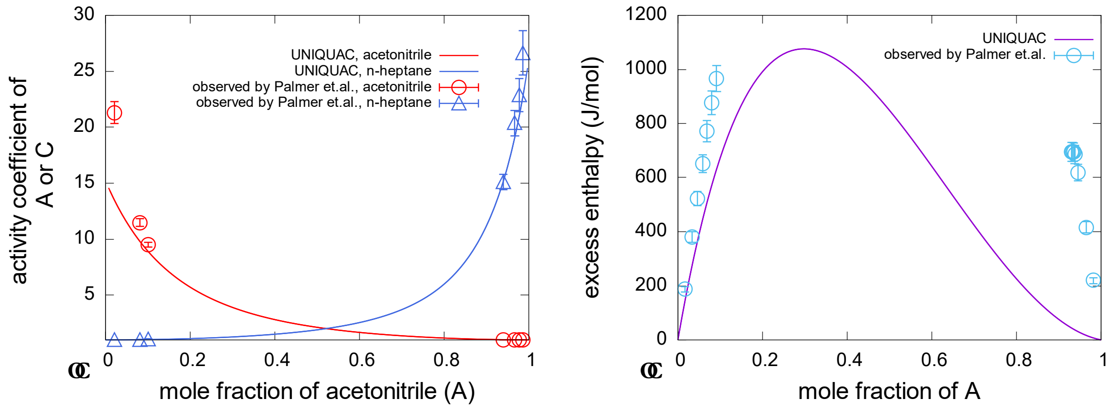
(c) T = 318 K

Figure 5.8: Excess enthalpy for the binary system acetonitrile (A) - benzene (B) at three different temperatures. Solid lines: calculated by OpenCalphad software with parameters assessed in this work, see Table 5.3; dash lines: calculated with parameters assessed by literature (Anderson and Prausnitz 1978), see Table 5.3; symbols: experimental data observed in literature (Nagata et al. 1982, Absood et al. 1976, Palmer and Smith 1972, Brown and Fock 1956, Di Cave et al. 1980).

and Fock 1956, Di Cave et al. 1980). The error bars of all the experimental data are estimated based on the error estimation made by D.A. Palmer, et.al. (Palmer and Smith 1972). Figures 5.7 and 5.8 show the comparisons between experimental and computational data at different temperatures. Two types of computed results are shown based on parameters from literature (Anderson and Prausnitz 1978) and parameters from this work.

From the comparison of the two figures, we conclude that the parameters in this work can predict the activity coefficients equally well as the literature parameters. However, excess enthalpies calculated with the parameters from this work are obviously more consistent with experimental data.

The interaction parameters for binary system, acetonitrile (A) - n-heptane (C), are calculated from experimental data (Palmer and Smith 1972). Literature values of the parameters (Anderson and Prausnitz 1978) are used as a starting point. When used with the UNIQUAC model implemented in the OpenCalphad software, the parameters from the literature could not be improved upon. Therefore, they are accepted in



(a) Activity coefficients (b) Excess enthalpy

Figure 5.9: Activities coefficients and excess enthalpy for the binary system acetonitrile (A) - n-heptane (C) at 318.15 K. Symbols: experimental data (Palmer and Smith 1972); lines: calculated with interaction parameters from literature (Anderson and Prausnitz 1978), see Table 5.3.

this work. The comparison with experimental data is shown in figure 5.9.

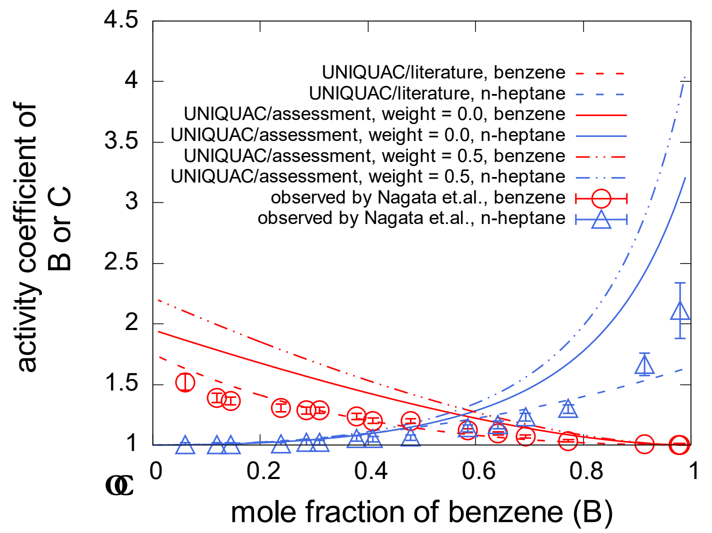
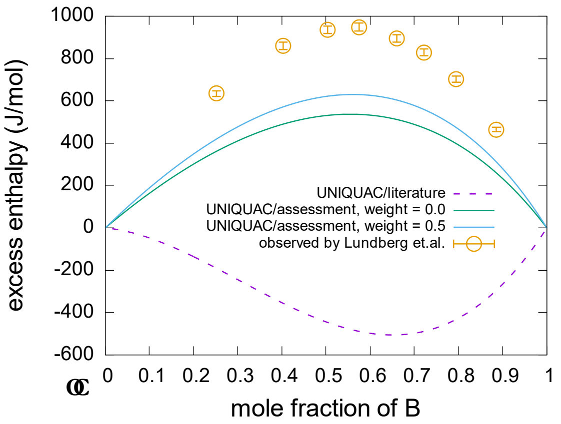
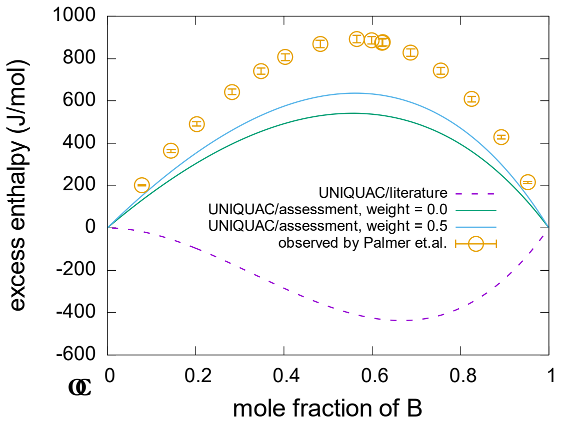


Figure 5.10: Activity coefficients for the binary system benzene (B) - n-heptane (C). Symbols: experimental data (Nagata and Nakamura 1987); dash lines: calculated with interaction parameters from literature (Anderson and Prausnitz 1978), see Table 5.3; dash lines with dots and solid lines: calculated with parameters from this work, see Table 5.3.

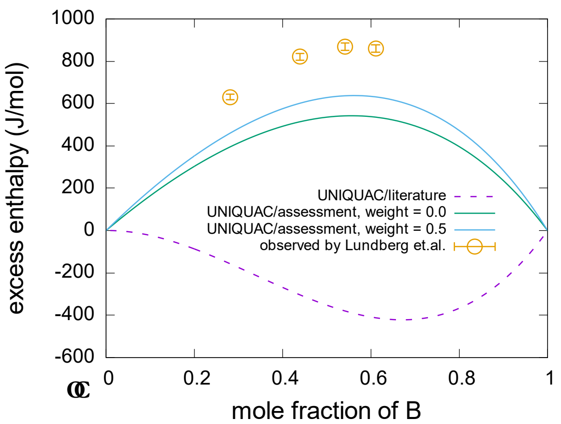
In contrast to the previous binaries, no set of parameters could be found that adequately represented both activity coefficients and experimental excess enthalpy data (Nagata and Nakamura 1987, Lundberg 1964, Palmer and Smith 1972) of the binary system benzene (B) - n-heptane (C). Therefore, two different weights, 0 and 0.5, are assigned to the experimental enthalpy data. The comparison between experimental and computational data for activity coefficients at 318 K and excess enthalpy at different temperatures is shown in figures 5.10 and 5.11, respectively.



(a) T = 298.15 K



(b) T = 318.15 K



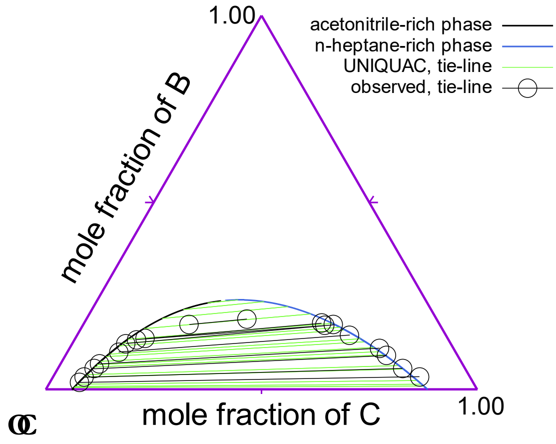
(c) T = 323 K

Figure 5.11: Excess enthalpy for the binary system benzene (B) - n-heptane (C) at different temperatures. Symbols: experimental data (Lundberg 1964, Palmer and Smith 1972); solid lines: calculated by OpenCalphad software with parameters assessed in this work, see Table 5.3; dash lines: calculated with parameters assessed by literature (Anderson and Prausnitz 1978), see Table 5.3.

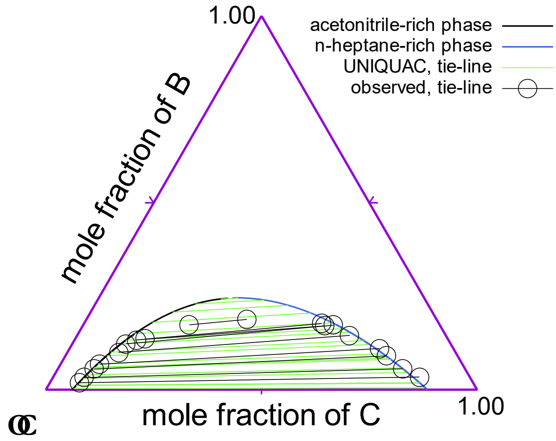
Ternary system

The prediction of ternary phase equilibria is a good way to assess the capability of binary interaction parameter estimations. Therefore, isothermal phase diagrams for the ternary system, acetonitrile (A) - benzene (B) - n-heptane (C), are calculated with the binary interaction parameter sets obtained in this work, see Fig. 5.12. Moreover, an isothermal phase diagram for this system calculated with the parameter set reported in the literature (Anderson and Prausnitz 1978) is shown in Fig. 5.4(a). When comparing the three figures, Fig. 5.12(a) shows the best agreement between the calculated and experimental tie-line data. This implies that the interaction parameter set, assessment 1, is the best of the three parameter sets in Table 5.3. Calculated results based on the binary interaction sets in Table 5.3 and experimental LLE for the ternary system at 318 K are shown in the Table 5.5.

It should be noted that the phase diagram from the literature, Fig. 5.4(a), was constructed using information from ternary tie-line data. In this work, on the other hand, the LLE ternary phase diagram is calculated using binary interaction parameters ob-



(a)



(b)

Figure 5.12: Isothermal phase diagrams at 318 K for ternary system acetonitrile (A) - benzene (B) - n-heptane (C) . Figure (a): calculated with interaction parameter set, assessment 1 in Table 5.3; Figure (b): calculated with interaction parameter set, assessment 2 in Table 5.3. Experimental data in both figures are from the work of Palmer et.al. (Palmer and Smith 1972).

tained from binary experimental data only.

5.6 Conclusion

The advantage of implementing the integral Gibbs energy expression and calculating chemical potentials and activity coefficients using a Gibbs energy minimizer like OpenCalphad is that thermodynamic consistency is guaranteed. For example, constraints such as Eq. 5.8 are automatically fulfilled. The UNIQUAC model has evolved since 1975 and there are additional residual terms that have been added. Inside the framework of OpenCalphad, it would also be possible to add excess terms; see, for example, Eq. 5.3.

This work makes the UNIQUAC model available in OpenCalphad, which simplifies the use of the UNIQUAC model for multicomponent phase diagram calculations, which is crucial for understanding the solubility of the mixture of reactants and solvents in the preparation of network polymers. It facilitates the use of thermodynamic properties like excess enthalpy and activity coefficients to assess the interaction parameters. Future applications include the possibility to combine calculations using the UNIQUAC model for the liquid phase together with the standard CALPHAD models for solid phases. In addition, this work could encourage applications of the UNIQUAC model to polymer systems by implementation of modified UNIQUAC models in the OpenCalphad software.

Table 5.5: Experimental and calculated LLE mole fraction for the ternary system acetonitrile (A) - benzene (B) - n-heptane (C) at 318 K. Interaction parameters from Table 5.3.

data type		n-Hexane-rich phase (I)		Acetonitrile-rich phase (II)	
		x_A	x_B	x_A	x_B
measured		0.1167	0.0342	0.9129	0.0188
calculated	literature	0.1286	0.0284	0.9158	0.0170
	deviation[a]	0.0119	0.0058	0.0029	0.0018
	assessment 1	0.1291	0.0286	0.9169	0.0168
	deviation	0.0124	0.0056	0.0040	0.0020
	assessment 2	0.1284	0.0276	0.9156	0.0179
	deviation	0.0117	0.0066	0.0027	0.0009
measured		0.1451	0.0562	0.8954	0.0325
calculated	literature	0.1387	0.0474	0.8994	0.0287
	deviation	0.0064	0.0088	0.0040	0.0038
	assessment 1	0.1394	0.0474	0.9010	0.0286
	deviation	0.0057	0.0088	0.0056	0.0039
	assessment 2	0.1381	0.0457	0.8987	0.0305
	deviation	0.0070	0.0105	0.0033	0.0020
measured		0.1642	0.0907	0.8605	0.0552
calculated	literature	0.1564	0.0765	0.8723	0.0475
	deviation	0.0078	0.0142	0.0118	0.0077
	assessment 1	0.1569	0.0761	0.8744	0.0479
	deviation	0.0073	0.0146	0.0139	0.0073
	assessment 2	0.1546	0.0735	0.8705	0.0512
	deviation	0.0096	0.0172	0.0100	0.0040
measured		0.1711	0.1104	0.8406	0.0684
calculated	literature	0.1673	0.0926	0.8562	0.0584
	deviation	0.0038	0.0178	0.0156	0.0100
	assessment 1	0.1676	0.0918	0.8584	0.0593
	deviation	0.0035	0.0186	0.0178	0.0091
	assessment 2	0.1647	0.0888	0.8535	0.0634
	deviation	0.0064	0.0216	0.0129	0.0050
measured		0.2225	0.1455	0.781	0.1002

calculated	literature	0.1925	0.1245	0.8209	0.0814
	deviation	0.0300	0.0210	0.0399	0.0188
	assessment 1	0.1915	0.1228	0.8229	0.0837
	deviation	0.0310	0.0227	0.0419	0.0165
	assessment 2	0.1870	0.1192	0.8158	0.0894
	deviation	0.0355	0.0263	0.0348	0.0108
measured		0.2466	0.1727	0.7529	0.1229
calculated	literature	0.2142	0.1472	0.7922	0.0993
	deviation	0.0324	0.0255	0.0393	0.0236
	assessment 1	0.2116	0.1449	0.7937	0.1029
	deviation	0.0350	0.0278	0.0408	0.0200
	assessment 2	0.2055	0.1409	0.7850	0.1098
	deviation	0.0411	0.0318	0.0321	0.0131
measured		0.2674	0.1709	0.7235	0.1333
calculated	literature	0.2179	0.1506	0.7875	0.1022
	deviation	0.0495	0.0203	0.0640	0.0311
	assessment 1	0.2149	0.1483	0.7888	0.1060
	deviation	0.0525	0.0226	0.0653	0.0273
	assessment 2	0.2087	0.1444	0.7797	0.1131
	deviation	0.0587	0.0265	0.0562	0.0202
measured		0.2723	0.1771	0.7025	0.1356
calculated	literature	0.2212	0.1536	0.7833	0.1047
	deviation	0.0511	0.0235	0.0808	0.0309
	assessment 1	0.2180	0.1513	0.7844	0.1088
	deviation	0.0543	0.0258	0.0819	0.0268
	assessment 2	0.2117	0.1475	0.7748	0.1163
	deviation	0.0606	0.0296	0.0723	0.0193
measured		0.4398	0.1882	0.5803	0.1737
calculated	literature	0.2500	0.1767	0.7474	0.1255
	deviation	0.1898	0.0115	0.1671	0.0482
	assessment 1	0.2433	0.1737	0.7484	0.1309
	deviation	0.1965	0.0145	0.1681	0.0428
	assessment 2	0.2343	0.1694	0.7380	0.1389
	deviation	0.2055	0.0188	0.1577	0.0348
NSSE for 9 sets of tie-line data					
literature		0.0048	0.0003	0.0047	0.0006
assessment 1		0.0052	0.0004	0.0048	0.0005
assessment 2		0.0058	0.0005	0.0040	0.0003

a: Here absolute values of the deviations are shown.

Symbols

a_i	activity of i, $a_i = \exp(\frac{\mu_i - \mu_i^\circ}{RT})$
G	total Gibbs energy, $G = G(T, P, N_i) = \sum_\alpha \aleph^\alpha G_m^\alpha(T, P, x_i^\alpha)$
G_m	molar Gibbs energy, $G_m = \sum_i x_i\ {}^\circ G_i +\ {}^{\mathrm{cfg}}G_m +\ {}^{\mathrm{res}}G_m$
G_m^α	molar Gibbs energy of α, $G_m^\alpha = G^\alpha/\aleph^\alpha = G_m^\alpha(T, P, x_i^\alpha)$
${}^\circ G_i^\alpha$	Gibbs energy of pure i in α
${}^{\mathrm{id}}G_m^\alpha$	ideal Gibbs energy model of α, ${}^{\mathrm{id}}G_m^\alpha = \sum_i x_i^\alpha(\ {}^\circ G_i^\alpha + RT\ln x_i^\alpha)$
${}^{\mathrm{M}}G_m^\alpha$	Gibbs energy of mixing of α, ${}^{\mathrm{M}}G_m^\alpha = G_m^\alpha - \sum_i x_i^\alpha\ {}^\circ G_i^\alpha$
${}^{\mathrm{E}}G_m^\alpha$	excess Gibbs energy of α, ${}^{\mathrm{E}}G_m^\alpha = G_m^\alpha -\ {}^{\mathrm{id}}G_m^\alpha$
${}^{\mathrm{cmb}}G_m^\alpha$	combinatorial Gibbs energy of α, ${}^{\mathrm{cmb}}G_m^\alpha = RT(\sum_i x_i^\alpha \ln(\frac{\Phi_i^\alpha}{x_i^\alpha}) + \frac{z^\alpha}{2}\sum_i q_i^\alpha x_i^\alpha \ln(\frac{\theta_i^\alpha}{\Phi_i^\alpha}))$
${}^{\mathrm{cfg}}G_m^\alpha$	configurational Gibbs energy of α, ${}^{\mathrm{cfg}}G_m^\alpha = RT(\sum_i x_i^\alpha \ln(\Phi_i^\alpha) + \frac{z^\alpha}{2}\sum_i q_i^\alpha x_i^\alpha \ln(\frac{\theta_i^\alpha}{\Phi_i^\alpha}))$
${}^{\mathrm{res}}G_m$	residual Gibbs energy
g^E	excess Gibbs energy
L_{ij}	binary interaction parameter between components i and j
N	total number of moles, $N = \sum_i N_i = \sum_i \sum_\alpha N_i^\alpha = \sum_\alpha \aleph^\alpha$
$\aleph^\alpha$	number of moles of phase α, $\aleph^\alpha = \sum_i N_i^\alpha$
N_i	number of moles of component i
N_i^α	number of moles of component i in phase α
NSSE	Normalized Sum of Squared Errors, $NSSE = \frac{\sum(x_{exp} - x_{calc})^2}{ND}$, ($ND$: number of data)
n_i	number of moles of component i
n_T	total number of moles
q_i	surface area of component i
r_i	volume of component i
w_{ji}	scaled interaction energy between i and j, $w_{ji} = \frac{\Delta u_{ji}}{R}$
x_i	mole fraction of component i, $x_i = \frac{N_i}{N}$
x_i^α	mole fraction of component i in α
z	number of nearest neighbors, $z = 10$
γ_i^α	activity coefficient of i in α, $\gamma_i^\alpha = \frac{a_i}{x_i^\alpha}$
Δu_{ji}	interaction energy between i and j, $\Delta u_{ji} = u_{ji} - u_{ii}$
θ	total surface area, $\theta = \sum_i x_i q_i$
θ_i	normalized surface area for i, $\theta_i = \frac{x_i q_i}{\theta}$
μ_i	chemical potential of i
ρ_i	interaction contribution to i
τ_{ji}	interaction between i and j
Φ	total volume, $\Phi = \sum_i x_i r_i$
Φ_i	normalized volume for i, $\Phi_i = \frac{x_i r_i}{\Phi}$